

TAILORING COMPOSITE SOLID PROPELLANTS TO PRODUCE A PLATEAU  
BURNING PROFILE

A Thesis

by

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## ABSTRACT

Presented in this thesis is the development of a new method to achieve plateau burning profiles in composite solid propellants. Propellants were formulated using ammonium perchlorate (AP) as the oxidizer and hydroxyl terminated polybutadiene (HTPB) for the binder and fuel. Unlike the linear relationship of a typical propellant, plateauing propellants will have a period of flat burning or pressure insensitivity, on a log-log plot. This phenomenon has been extensively studied to determine the cause of the plateau effect; the known methods limit the formulations to a few well developed batches. There are three main mechanisms responsible for the plateauing behavior, in particular, the binder melt layer, oxidizer combustion as a monopropellant, and catalyst effects. This thesis examines previous methods to formulate plateau propellants, and then introduces new methods to achieve a plateau propellant.

Propellants were formulated using various AP sizes and size distributions along with a non-catalytic additive. The baseline propellant consisted of both 80% monomodal and 85% bimodal AP and 20% or 15% binder composed of isophorone diisocyanate (IPDI)-cured HTPB with Dioctyl Adipate. A trimodal mixture was introduced with oxidizer mass loading at 85% and 15% binder concentration. Propellant burning rates were tested using a strand bomb pressurized at varying conditions between 500 and 3000 psi. Catalytic additives were also introduced to the propellant to improve the burning rate, and in this study titania was chosen for its

uniformity and reliability. First, baseline propellants with wide AP distributions were made to check the plateau effect with AP. Then, a non-catalytic additive was added to promote the plateau effect. Once the plateau additive was proven to be effective, titania was introduced to the propellant formulation to observe how the nano-additive affects the plateau behavior.

Analysis of various propellant formulations determined that plateau is most easily achieved through a wide size distribution of AP, but can also be obtained with a narrower AP distribution using an additive. When titania is added to the formulation, the plateau effects could be reduced or eliminated. The mechanism that best describes the ability for a propellant to plateau is the melt layer theory. This theory describes how the melt layer causes the AP to retreat in the melt layer and confines the oxidizer crystals preventing the proper mixing of combustion gases in the three-flame structure. The additive is believed to lower the viscosity, allowing more oxidizer to recess into the binder. Plateau is also achieved with the addition of burning rate modifier titania, but in small concentrations.

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## NOMENCLATURE

a	Temperature Coefficient
AMPAC	Advanced Materials Processing and Analysis Center
AP	Ammonium Perchlorate
APCP	Ammonium Perchlorate Composite Propellant
BDP	Beckstead-Derr-Price
DOA	Dioctyl Adipate
DDI	Dimeryl Diisocyanate
HTPB	Hydroxyl-Terminated Polybutadiene
IPDI	Isophorone Diisocyanate
n	Combustion Index/Pressure Exponent
NC	Nitrocellulose
P	Pressure
PBAA	Polybutadiene Acrylic Acid
PBAN	Polybutadiene Acrylonitrile Acrylic Acid
PU	Polyurethane
r	Burning Rate
SEM	Scanning Electron Microscope
TAMU	Texas A&M University
TiO <sub>2</sub>	“Titania” or “Titanium Dioxide”

UCF

University of Central Florida

## TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
ACKNOWLEDGEMENTS .....	iv
NOMENCLATURE.....	v
TABLE OF CONTENTS .....	vii
LIST OF FIGURES.....	viii
LIST OF TABLES .....	x
1. INTRODUCTION.....	1
1.1 Solid Propellant Fundamentals.....	1
1.2 Burning Propellants.....	3
2. BACKGROUND.....	16
3. PROPELLANT FORMULATIONS .....	25
3.1 Propellant Formulations .....	25
3.2 Propellant Mixing.....	30
4. TESTING PROCEDURES .....	34
4.1 Test Vessel .....	34
4.2 Sample Preparation .....	35
4.3 Testing and Data Acquisition.....	38
5. DATA PROCESSING AND UNCERTAINTY .....	42
5.1 Data Processing .....	42
5.2 Uncertainty Analysis .....	43
6. PLATEAU PROPELLANT DATA .....	45
7. CONCLUSION .....	52
REFERENCES.....	54

## LIST OF FIGURES

	Page
Figure 1 An illustration of the various known burning rate profiles found in literature. ....	5
Figure 2 Pressure and burning rate plots for the combustion chamber of a rocket motor with stable operating conditions. Pressure and burning rate plot with an extreme pressure oscillation of 10% peak to peak. ....	7
Figure 3 Pressure and burning rate plots for the combustion chamber of a rocket motor with unstable operating conditions. ....	10
Figure 4 Burning rates for both plateau- (top) and mesa- (bottom) propellants with the same pressure fluctuations observed in Fig. 2.....	12
Figure 5 Outline of the Tests performed in the laboratory.....	14
Figure 6 Standard one-dimensional flame structure over the surface of a burning propellant. ....	18
Figure 7 Simple illustrations for how the melt layer rises over the AP crystals limiting the rate of combustion.. ....	20
Figure 8 Combustion of a solid propellant with the addition of both a catalyst and the plateau additive.....	24
Figure 9 AP size distributions provided by Fluid Energy Corp. ....	27
Figure 10 Solid propellant test samples did not vary in appearance when comparing the baseline with the additive. ....	29
Figure 11 Image of a laboratory-scale, hand-mixed AP-HTPB propellant.....	31
Figure 12 Strand-bomb test vessel. ....	34
Figure 13 Propellant sample in Teflon® sheath.....	36
Figure 14 Propellant strand-holder photograph and schematic demonstrating how the propellant is mounted and the wire is set upon the propellant. ....	37



Figure 15 Experimental schematic for solid propellant burning rate remote tests.....	39
Figure 16 Sample pressure and light-emission data plot taken from experiments. ....	41
Figure 17 Plot of the 80% baseline using a wide distribution of AP compared to the typical sieved AP batch.. ....	46
Figure 18 Propellant using 85% bimodal mixture with the additive to initiate the plateau effect using a wide AP distribution. ....	47
Figure 19 Propellant using 85% bimodal mixture with the additive to initiate the plateau effect using a normal AP distribution. ....	48
Figure 20 Propellant with sieved AP at 85% using the non-catalytic additive with both bimodal and trimodal mixture to plateau the propellant. ....	49
Figure 21 Results from the plateau additive combined with the titania to check if plateau could have an elevated burning rate.....	50

## LIST OF TABLES

	Page
Table 1 Overview of propellant formulations used in this thesis study. ....	14
Table 2 Propellant formulations used in this thesis study. ....	30
Table 3 Uncertainty calculated from the comparison of the theoretical density and the actual density of the propellant. ....	44

## 1. INTRODUCTION

### 1.1 Solid Propellant Fundamentals

Solid propellants contain both fuel and oxidizer in a heterogeneous mixture that is cast into motors and upon ignition, are capable of self-sustained combustion.

Applications for these propellants span multiple industries: from the use in heavy lift space flight and propulsion systems for missiles to the inflation systems for automobile airbags, and numerous other applications in each particular industry. Burning propellants produce high-temperature and -pressure gases for propulsion purposes that flow from a combustion chamber and out a nozzle to convert the chemical energy to thermal energy and ultimately into useful kinetic energy. Solid rocket propellants can be grouped into various categories based on the class and solid interactions of the chemical components involved.

Two common classifications for solid propellants are *nitropolymer* and *composite* propellants, with the primary difference being the presence of nitrocellulose (NC). Nitropolymer propellants will typically have the oxidizer chemically bound to the fuel in the form of O-NO<sub>2</sub> bonds, whereas composite propellants have the oxidizer in a heterogeneous mixture with the binder to form the propellant [1]. Composite propellants have their crystalline oxidizer mixed heterogeneously with the liquid binder and may contain metals and metal oxide catalysts to improve performance. In composite propellants, the binder is a polyurethane (PU) or polystyrene, such as polybutadiene

acrylic acid (PBAA), polybutadiene acrylonitrile acrylic acid (PBAN), or hydroxyl-terminated polybutadiene (HTPB). Composite propellants in this thesis focused on the use of ammonium perchlorate (AP) as the crystalline oxidizer, HTPB as the hydrocarbon binder-fuel, and titanium dioxide ( $\text{TiO}_2$ ) as the catalyst used to improve the burning rate.

Ammonium perchlorate (AP:  $\text{NH}_4\text{ClO}_4$ ) is used as the oxidizer in composite solid propellants due to its availability and its high oxygen content [1]. Other typical oxidizers include ammonium nitrate and potassium perchlorate, which are either not as effective or are less stable compounds. Oxidizers and metal catalysts are suspended in the binder and a fuel. The Petersen Research Group at Texas A&M University has been making propellants consisting of a single size of AP, termed *monomodal*, as well as propellants consisting of an oxidizer of two distinct sizes, termed *bimodal*. A new *trimodal* propellant mixture was formulated in this study, consisting of three differently sized batches of AP particles. The specific binder chosen was R45M-HTPB for its extensive use and the reduced smoke aspect of the propellant. A curing agent was used with AP-HTPB propellants to harden the propellant slurry for casting, and isophorone diisocyanate (IPDI) was utilized to cast the propellant. There is a short time during which the propellant can be cast into various molds—either for testing or for practical uses—before the propellant slurry solidifies to its final structure. Once the curative agent is added, the hydroxyls are removed from the end of the polymer chain and the curing process begins, with elevated temperatures accelerating the process.

In addition to the base ingredients, various additives can be introduced to increase the performance, processability, or strength of a propellant to tailor it for various applications. Numerous studies have shown that certain transition metal oxides (TMO) can act as significant catalysts for enhancing the thermal decomposition of AP. When these additives are introduced into composite propellants, they have the potential to significantly increase the burning rate [2, 3]. The study of propellant additives has been the focus of research in the propellants studies for years.

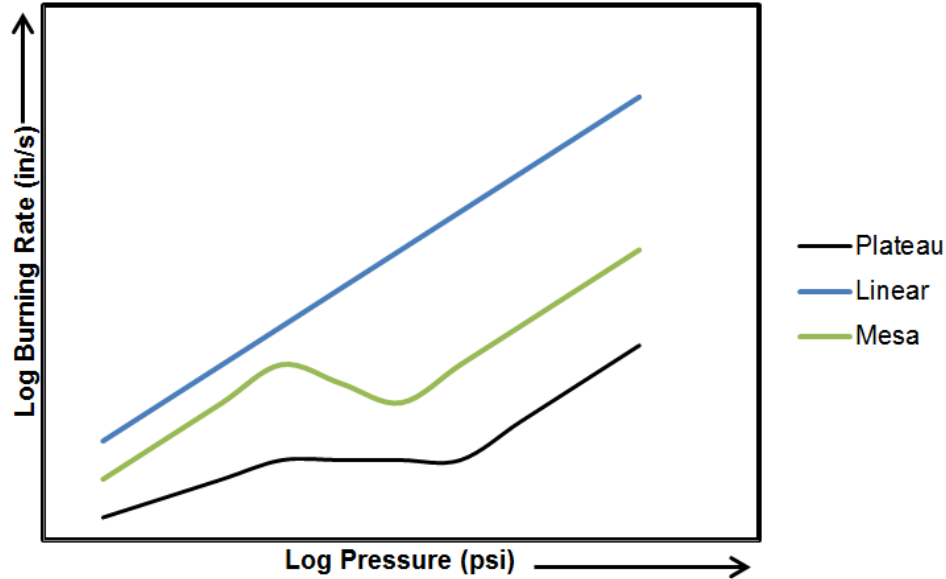
## **1.2 Burning Propellants**

Studying the combustion of propellants is of great importance in the propulsion industry. Knowing how the propellant will behave under various burning conditions dictates which propellant should be used for the desired propulsion system. Propellant applications vary for the type of propulsion needed, such as high thrust for heavy lift and high efficiency for orbit and upper-stage space vehicles. When studying solid propellants, knowing how the burning rate changes with pressure is of the utmost importance. Burning rate correlations are typically expressed as a power law shown in Eq. 1 [1, 2]. This relation is known as either St. Robert's law or Vieille's law and appears linear when plotted on a log-log scale.

$$r = aP^n \quad (1)$$

In the above equation,  $a$  represents the temperature coefficient which accounts for the variation in the initial temperature and  $P$  represents pressure. The pressure exponent  $n$  is also known as the combustion index and provides a measurement of the sensitivity of the burning rate to chamber pressure. A propellant formulation with a pressure index close to one can cause large fluctuations in the chamber pressure as the burning area varies during burning. Propellants with a pressure index value less than one are typically chosen since they result in less drastic fluctuations in chamber burning rate due to natural fluctuations in the chamber pressure.

As previously mentioned, a standard propellant will appear to have a linear burning rate relationship with pressure on a log-log plot of the two variables. Other common propellant burning behaviors found in the literature include plateau- and mesa-burning profiles. Plateauing propellants typically have burning rates that increase with pressure at lower pressures, then—at a pressure region set by the propellant formulations—their burning rate correlations will level off and have (ideally) no change with pressure. The burning rates will exhibit pressure insensitivity until the pressure is elevated out of the plateau region, where the burning rates will begin to rise with pressure. This phenomenon was first discovered by Steinz et al. [3] at Princeton University in their research throughout the 1960s. Figure 1 illustrates that mesa burning is similar to plateau burning, but takes a distinctly negative slope from which the propellant also recovers at higher pressures instead of the temporary region of leveled-off burning rates [4].

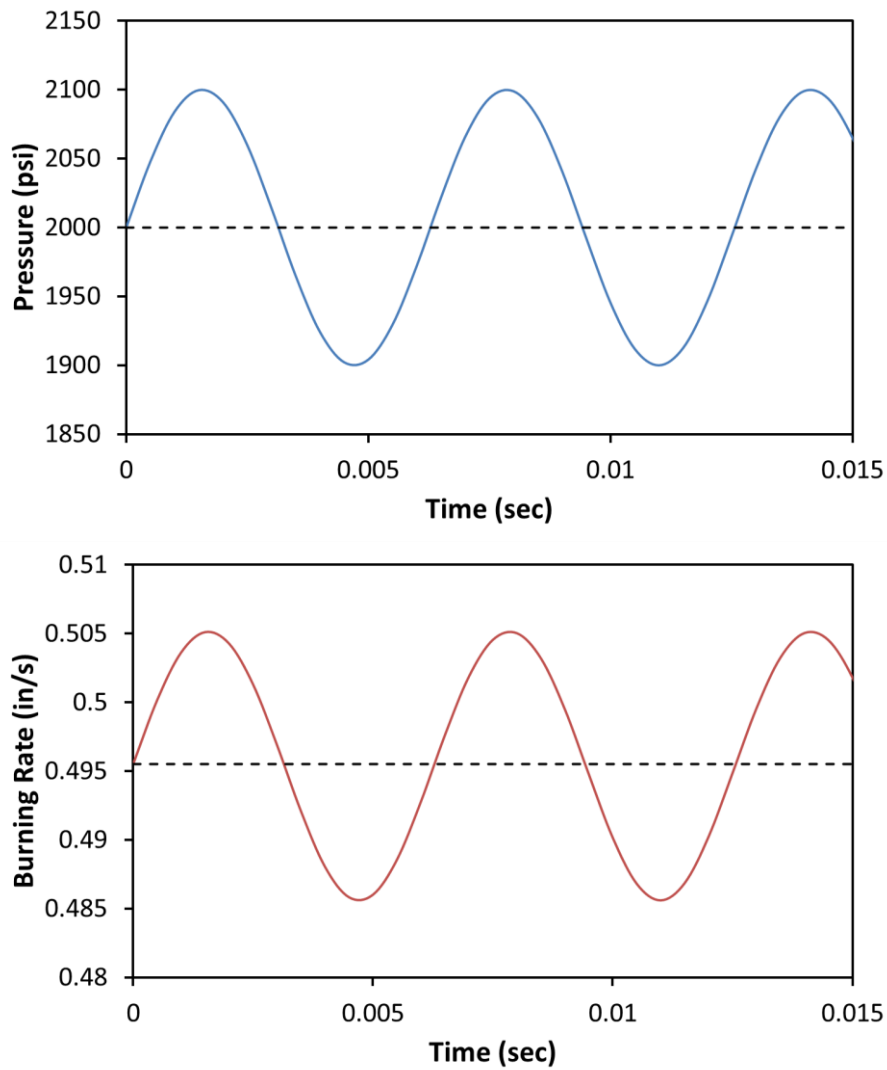


**Figure 1** An illustration of the various known burning rate profiles found in literature.

Knowing that the burning rate is dependent on the pressure in the combustion chamber, solid propellants are known to cause fluctuations in pressure that render them less desirable for human flight. This thesis investigates the methods in the literature used to produce a plateauing burning profile in solid propellants and explores some new formulations. One of the biggest concerns when talking about solid propellants is the pressure stability of a given formulation. A discussion on the stability is presented as follows to provide the purpose for a study of plateauing propellants. Low pressure oscillations in the combustion chamber result in a minimal impact on the burning rate. For such a case, there is little fluctuation in the burning rate, thus the effects of the fluctuation can be neglected as the pressure oscillates at 0.1% of the mean chamber

pressure at a frequency of 1000 Hz in the combustion chamber. Burning rates with a low pressure and burning rate oscillation is representative of propellant which experiences acceptable pressure changes. However, when the chamber pressure fluctuates by 10% for a propellant with a positive pressure exponent at frequency of 1000 Hz, the burning rate will have a noticeably larger change. Figure 2 demonstrates a simple 10% fluctuation in the combustion chamber and its effects on the burning rate of the propellant. The pressure oscillation is generated using a simple sinusoidal function with the 1000 Hz frequency of oscillation to serve as an example for how the pressure could oscillate. For both pressure oscillating plots the value of temperature constant  $a$  is 0.025 and the value of pressure exponent  $n$  is 0.394, which is taken from a typical baseline propellant.





**Figure 2 Pressure and burning rate plots for the combustion chamber of a rocket motor with stable operating conditions. Pressure and burning rate plot with an extreme pressure oscillation of 10% peak to peak.**

Pressure oscillations of 100 psi are observed in the above plots and significantly impact the combustion conditions for the solid propellant. With fluctuation in the burning rate as large as 10%, the resonance effect cannot be ignored, and the increase in the burning

rate will feed back into the pressure of the combustion chamber. With a plateau propellant, the burning rate would remain constant, much like the burning rate in Fig. 3 above. Unlike liquid propellants, solid propellants are not able to be throttled since they are not pumped into the combustion chamber. They are instead cast into the chamber, and the mass flow rate is determined by the propellant burning rate. For solid propellants, the mass flow rate is dependent on the burning rate of the propellant by Eq. 2. A change in the burning mass flow rate ( $\dot{m}_p$ ) will feed back into the pressure using Eqs. 3 and 4 knowing that the mass flow rate at the throat ( $\dot{m}_t$ ) will remain constant the time rate of change of the mass in the system will fluctuate [2].

$$\dot{m}_p = A_b r p \quad (2)$$

Where,

$$\frac{dm_{cv}}{dt} = \dot{m}_p - \dot{m}_t \quad (3)$$

$$m_{cv} = \frac{P_o(t)}{RT_o(t)} V \quad (4)$$

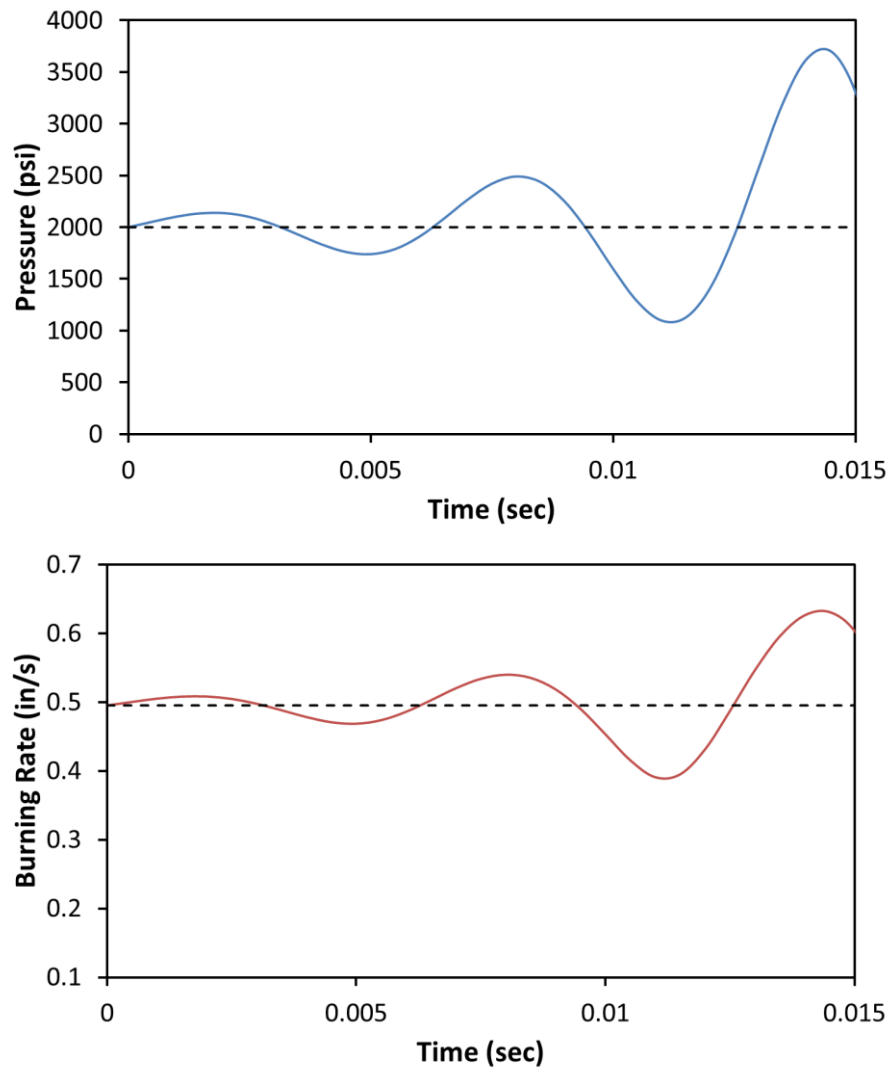
Resulting in the relationships for pressure and burning rate given by Eqs. 5 and 6 for any given propellant formulations [1]. The value of  $\phi$  is the 10% peak-to-peak amplitude and the  $\omega$  is the 1000 Hz frequency. The  $P_c$  is the initial chamber pressure of 2000 psi.

$$P(t) = P_c + \phi e^{at} \cos \omega t \quad (5)$$

$$r(t) = a(P_c + \phi e^{at} \cos \omega t)^n \quad (6)$$

If the combustion chamber has a spike that elevates the chamber pressure, the burning rate will rise to cause an increased mass flow rate, thereby increasing the chamber

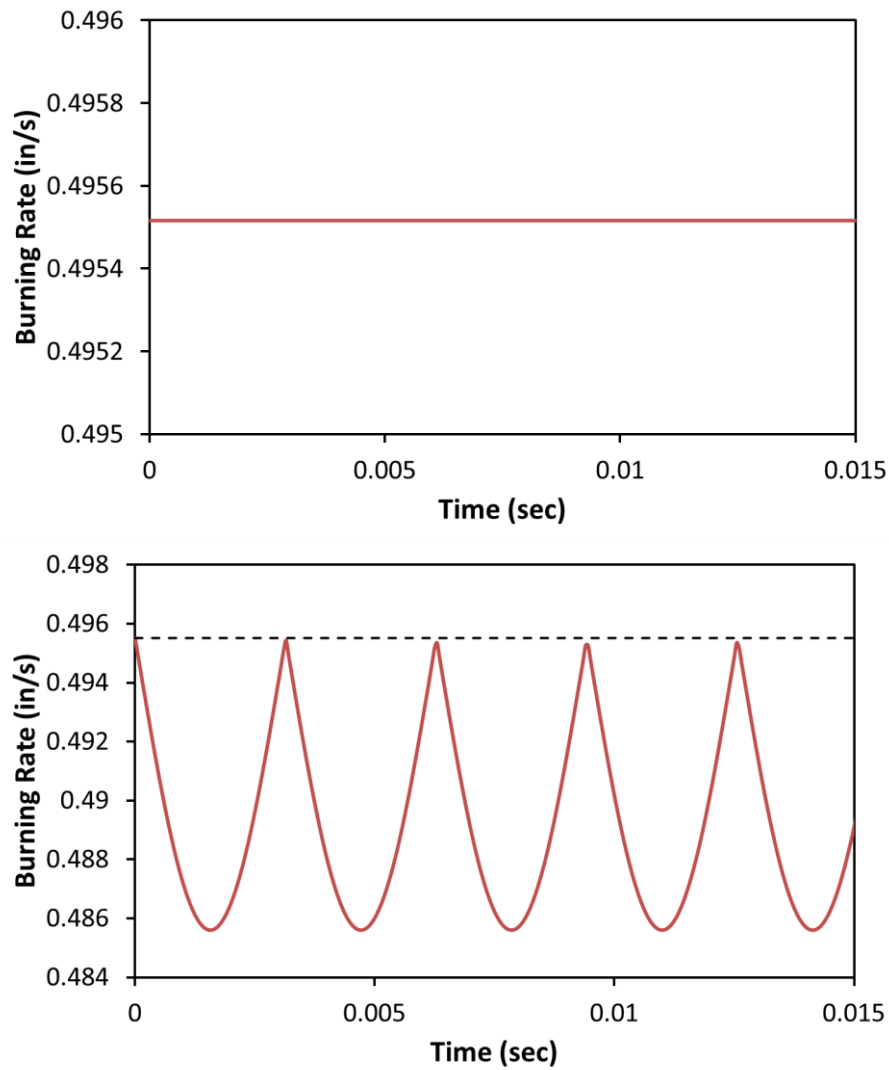
pressure further. The effects of this pressure feedback from the propellant burning rate can be viewed in Fig. 4. As the pressure increases, the burning rate fluctuates causing a change in the combustion chamber creating a feedback loop. Oscillations are created using the same sinusoidal behavior, with the addition of an exponentially increasing value determined from the propellant characteristics. With the feedback loop added to the analysis, the pressure will oscillate with an unsteady increase in amplitude. The oscillating pressure will reach a point where the combustion chamber will rupture, or the propellant will not provide enough thrust to sustain flight. If a rupture in the combustion chamber results in a rapid loss of pressure, combustion of the propellant may cease altogether.



**Figure 3 Pressure and burning rate plots for the combustion chamber of a rocket motor with unstable operating conditions. Pressure and burning rate plots show the effect of the increased burning rate on the pressure. At drastically large increase in pressure will likely damage or destroy the motor.**

The effects of pressure oscillations seen above could be remedied with a plateau or mesa propellant, because their burning rates would remain the same in the plateau case or drop

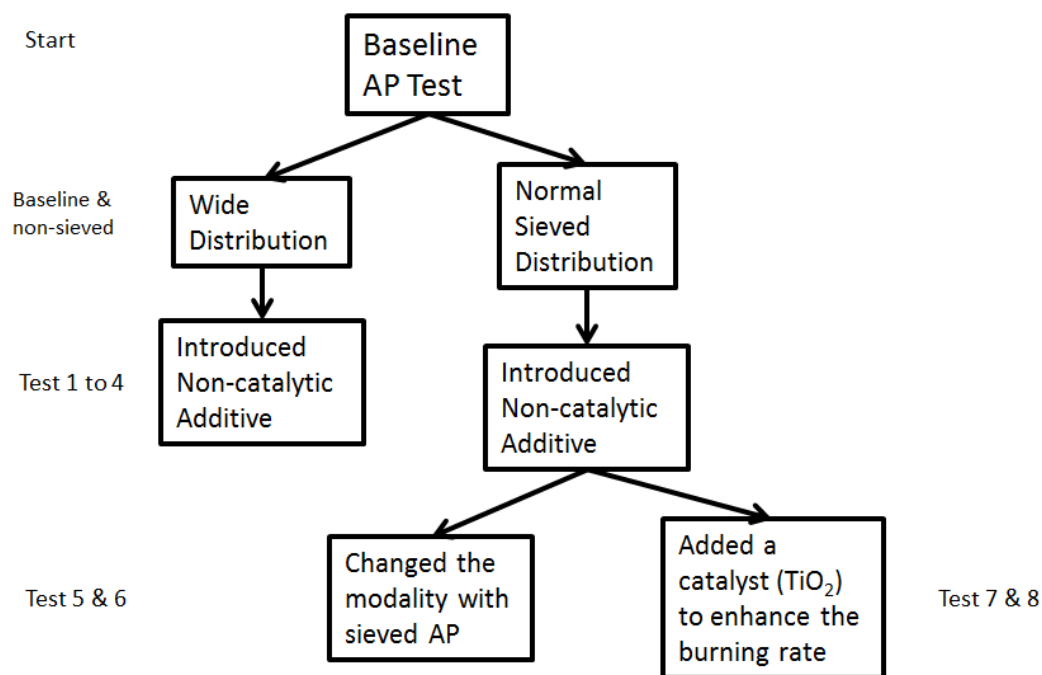
for a mesa propellant. A plateau propellant will have a pressure oscillation like in Fig. 3, but the burning rate will not change with pressure because it is constant. With a mesa propellant the oscillation will slow the burning rate dropping the pressure which would bring the burning rate back to its desired rate. Examples of these burning rates are seen in Fig. 4 where the burning rate remains constant.



**Figure 4 Burning rates for both plateau- (top) and mesa- (bottom) propellants with the same pressure fluctuations observed in Fig. 2**

Either way, the limited burning rate effects of plateau and mesa propellants that resonate back into the combustion chamber would ideally prevent a drastic change in chamber pressure from ever occurring.

Combustion stability is of the utmost importance when it comes to propulsion, especially when designing for human flight. Propellants must be designed in a way that prevents oscillations in the pressure from adversely affecting the burning rate of the propellant. One known method of ensuring combustion stability is using a plateau propellant at the specific pressure range where its burning rate is known to be insensitive to pressure. A plateau propellant would experience burning oscillations similar to what is seen in Fig. 2. The mesa propellant would also be useful, since the burning rate would prevent the out of control burning seen in Fig. 3; a mesa propellant would slow the burning rate when the pressure spiked. Klagger and Zimmerman of GenCorp/Aerojet Solid Propulsion company stated that a quality plateau solid propellant could be effectively utilized in “a lightweight rocket motor . . . with benefits such as higher specific impulse, more neutral pressure-time curves, more safe conditions to minimum pressure fluctuations, and constant area ratio” [3]. The nature of this thesis is to present the work performed at Texas A&M University on the development of plateau propellants through varying AP concentration and using a non-catalytic additive. Figure 5 outlines the testing procedure used in this study, varying the propellant formulations and table 1 gives the specific propellant formulations tested.



**Figure 5 Outline of the Tests performed in the laboratory.**

**Table 1 Overview of propellant formulations used in this thesis study.**

Propellant	AP%	Modality	Catalyst	Plateau Additive
Baseline	80%	Monmodal	-	No
Baseline	85%	Bimodal	-	No
Unsieved	80%	Monmodal	-	No
Batch 1	85%	Bimodal	-	Yes
Batch 2	85%	Bimodal	-	Yes
Batch 3	85%	Bimodal	-	Yes
Batch 4	85%	Bimodal	-	Yes
Batch 5	85%	Bimodal	-	Yes
Batch 6	85%	Trimodal	-	Yes
Batch 7	80%	Monmodal	1.00%	Yes
Batch 8	80%	Monmodal	0.10%	Yes



Using a wide AP distribution, the intent is to recess more of the AP particles into the binder melt layer, resulting in plateau burning within the tested pressure range of 500 to 2500 psi. A non-catalytic additive is applied to reduce the viscosity of the binder melt layer and promote more oxidizer recession within the melt layer. Similar combustion improvements were made using bimodal and trimodal mixtures as well. The study concludes with the addition of titania to the propellant formulations to enhance burning rates and alter the positions of burning rate plateaus, allowing the author to determine whether or not titania can be added to a plateau propellant and still permit the iconic plateau behavior. Chapter 2 contains the background work used in this thesis on the development of plateau propellants. Propellant formulations are then presented in chapter 3 followed by the testing procedures and data processing methods.

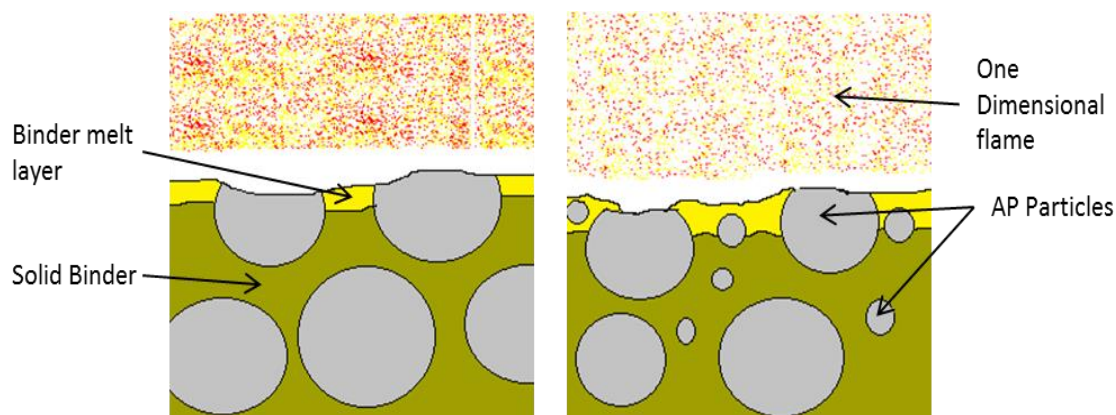
## 2. BACKGROUND

The direct study of plateau propellants has been an ongoing area of research over the during couple of decades. One goal of this literature review is to present the previous work performed on plateau propellants. By presenting previous work, the background is provided allowing the reader to verify whether or not the newly formulated theories in this thesis agree with the current working theories. From the past research, the plateau effect can be attributed to three main factors: binder melt layer, oxidizer burning behavior ( burning as a monopropellant), and additive influence. Each mechanism is then utilized in the development of new plateau propellant formulations.

The binder melt layer theory states that when the propellant burns, the binder melts creating a layer of molten liquid binder. When the binder melts, the oxidizer crystals begin to sink to the bottom of the molten binder until the liquid binder submerges the oxidizer crystal to a point of limited burning. This thesis picks up where Stephens left off regarding nanoparticles used in plateau propellants [4]. Plateau burning has existed for a long time and was widely seen in the propellant industry, as evidenced by an early NASA report on propellant selection [5], but there was a lack of published information initially. Research on plateau propellants was first performed by Summerfield at Princeton University in the late 1960s. While working on a one-dimensional model for composite propellant combustion, the Granular Diffusion Flame Model, Summerfield and coworkers proposed several instrumental deductions on the

cause of plateau burning as well as multiple, significant observations [6]. One key observation was the notion of the molten binder melt layer having an influence on the plateau by slowing the combustion within a specific pressure range. Molten binder would flow over the surface of the AP crystal and impede the pyrolysis of the oxidizer. Further studies showed that the binders that readily melt, such as polyurethane (PU) and polystyrene, would create the most dramatic melt layer behavior, but binders that are relatively more difficult to melt, such as polybutadiene acrylic acid (PBAA) and polybutadiene acrylonitrile acrylic acid (PBAN), could also produce such behaviors, but to a more limited degree [7-12]. The use of the various binders was an effort to define multiple physical parameters for each. Also, the thickness of the melt layer was shown to change depending on the curative used to cast the propellant for the various binders previously mentioned. Several groups studied the melting behavior of hydrocarbon binders in a hot stage microscope [8-12].

In order to a better understand how the binder melt layer affects the burning surface of the propellant, a schematic for the burning surface can be drawn. Figure 6 illustrates the binder melt layer over the surface of the propellant for a one-dimensional flame structure. In the image on the left, the melt layer is shown to surround the AP particle during combustion of a baseline propellant with a single AP particle size. The image on the right represents a propellant with a wide distribution of AP and the binder melt layer is observed to be partially running over the top of the AP particle, slowing the combustion.

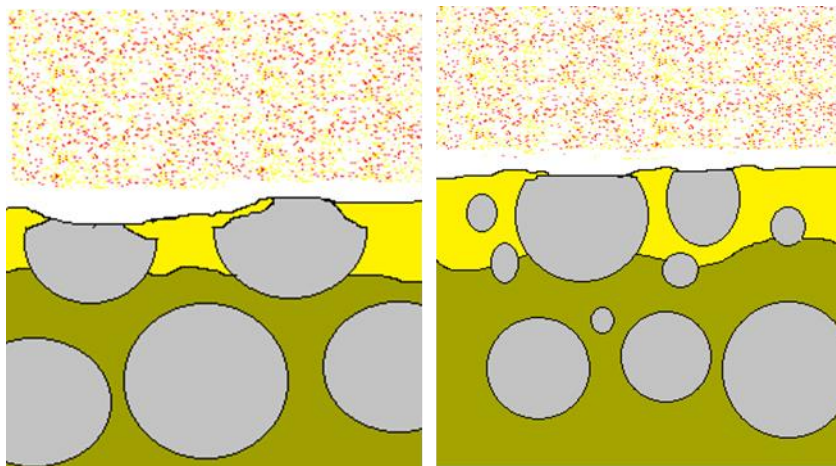


**Figure 6 Standard one-dimensional flame structure over the surface of a burning propellant. The image on the left illustrates a monomodal baseline with a normal particle size distribution. The image on the right illustrates how the melt layer covers the smaller AP particles for a wide-distribution AP batch.**

Studying binders and binder curatives is important to determine if one has a binder melt layer that is more conducive to plateau burning than the other. The binder systems (polybutadiene-acrylonitrile-acrylic acid terpolymer, PBAN, isophorone diisocyanate, IPDI-cured HTPB and dimethyl diisocyanate, DDI-cured HTPB) differed markedly in melt temperature and viscosity. For HTPB binders, the melt characteristics varied with the curative used. DDI-cured HTPB melted at 260°C to a low viscosity fluid and is considered to be a “high melt” binder. Whereas IPDI-cured HTPB melted more slowly over a range of temperatures from 330-370°C. The lower melt temperature of the DDI-cured binder material gives rise to a thicker melt layer in the propellant. As the temperature approached 500°C, the melt started to bubble, and both decomposed over a 10°C temperature range around 500°C, the temperature of the burning surface.

SEM and cinematography were used on samples to observe the melt layer, where bubbling in the liquid material was observed at the burning surface [12-17]. Cohen and Hightower [18] published a paper addressing and explaining plateau burning using a literature review and a propellants comparison used by different recognized groups. Various propellants were studied and expounded upon resulting in additional information on plasticizer and solid additive comparisons [19-23]. The result of these studies placed a heavy emphasis on the viscosity of the melt layer rather than the thickness. The lower viscosity can explain the recession of the particle in the melted binder giving rise to areas for further exploration.

The present study introduced an additive which noticeably lowered the viscosity of the propellant during mixing; this lower unheated viscosity likely results in a similarly lower melt layer viscosity. By adding an additive which lowers the viscosity of the melt layer, the AP particles are able to fall at an increased velocity allowing for the HTPB binder to smother the AP crystals at an increased rate. By examining the densities of the AP and binder, it is believed that the large density of the AP would sink within the binder. Figure 7 depicts how the additive lowers the viscosity of the propellant, allowing for the AP to recess into the melt layer. When the smaller particle recess, the binder melt layer flows over the top of the AP particles from a simple volume displacement of the smaller AP particles, slowing the combustion process. When the AP consists of larger, uniform particles, the melt layer is not thick enough to drastically influence the rate of combustion.



**Figure 7 Simple illustrations for how the melt layer rises over the AP crystals limiting the rate of combustion. The left image is of a monomodal propellant with the non-catalytic additive, and the image on the right is of a multi modal mixture with the same additive.**

The image on the left illustrates how the lower-viscosity melt layer smothers the AP particles pyrolysis to a slower rate of combustion of a monomodal propellant. A multimodal propellant is shown on the right to provide an example of how the smaller particles can better be inhibited by the lower viscosity of the melt layer. With a lower viscosity, the small particles can drop away from the burning surface.

A second mechanism used in the description of the plateau effect is the oxidizer contribution. In 1969, Boggs presented his work on a four-regime description on the deflagration of a single AP crystal [24], resulting in a description on the combustion of an AP oxidizer crystal. AP burns as a monopropellant in a way that is limited in its ability to sustain combustion within a given pressures region. Limiting the combustion

of AP allowing for the melt layer of binder to further hinder AP decomposition aligns well with the pressure region similar to that of a plateau propellant.

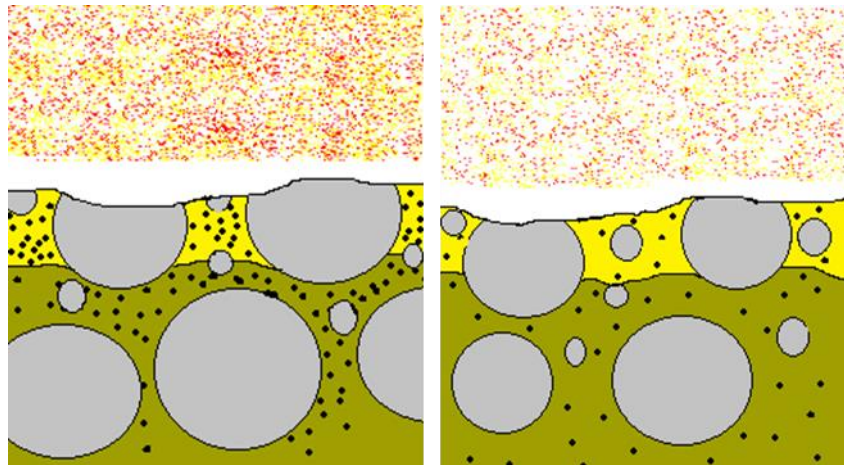
In the early 1970's Beckstead et al. developed and published the famous BDP (Beckstead–Derr–Price) model based on multiple flame structures describing the combustion of the AP crystal [25]. The introduction of the model spurred research to study the characterization of the AP particle size distribution. Papers were then released showing that the oxidizers with both bimodal and trimodal distributions could cause plateauing behavior if small particle sizes were used (6, 20, and 200  $\mu\text{m}$ ) [19-23]. Another study released by the Defense Research Centre in Salisbury, Australia showed that formulas made with a wide distribution of AP particles had higher ability to produce plateau propellant burning curves. From the results of the study, Fong and Smith observed that coarse-to-fine oxidizer ratios of 60:40 or greater had a higher chance of producing a plateau-burning propellant [26]. As indicated by the past studies, the characteristics of the oxidizer play important roles in the propellant's burning behavior. With smaller particles, the oxidizer effects on the plateau propellant are directly related to the melt layer by the idea that the smaller AP particles are overrun by the melted binder. These effects are best seen in the image on the right of Fig. 6, the wide-AP-distribution propellant. This thesis provides the AP sizing information to enhance the information behind the data collected since this characteristic has been shown to be very important.

The final mechanism that has been used to describe the plateau propellant is the additive influence on the propellant burning behavior. Additives are often used in propellants to enhance the burning rate seen in various propellant formulations. Some studies have shown that the inclusion of a catalytic additive can also increase the occurrence of plateau burning. This effect was seen in a couple of the studies performed by Strahle and coworkers, on the addition of ferrocene, iron blue, and copper chromite [27, 28]. While their study demonstrated that the catalyst enhanced the burning rate, it also led to the first important binder observations on how the catalyst affected the melt layer. The study showed that the catalyst increased the viscosity in the binder melt layer, resulting in reduced thickness of the melt layer was reduced. At lower pressure, there was a significant physical or chemical effect in the removal or inhibition of the binder melt flow.

Cohen et al., in an effort to characterize binders to be used in the BDP model, found that catalysts in the HTPB binder only affected the combustion of the AP oxidizer or the gas-phase reaction of AP and HTPB [11]. Brill and Budenz [29] from the University of Delaware published a study on the catalytic behavior of  $\text{TiO}_2$  as an additive to produce plateau-burning-rate curves. The proposed theory is that the titania increases the thickness of the binder melt layer. A model was developed by Frazier at Texas A&M University that can be used to help predict the influence of nanoparticles on the burning rate of composite propellants. The model confirmed the theory that the catalyst only affects the AP crystal and provided evidence that the addition of titania



increases the oxidizer melt layer [30]. The addition of a burning rate enhancer has been shown in the past to increase the oxidizer melt layer for given pressures; inhibiting the plateau burning profile by allowing for AP to melt and combust faster layer rather than to settle under the HTPB melt layer. This study examined two different concentrations of catalyst. While the catalyst increases the oxidizer melt layer, the viscosity is increased. With the use of a non-catalytic additive, the melt layer viscosity can be reduced allowing for greater possibility for plateau behavior. Figure 8 is a simple illustration of how both additives increase the melt layer on the propellant surface during combustion. With the higher concentration of the nano-scale titania, the recession of the smaller AP crystals is limited and more of the fine AP is available to participate in combustion. The melt layer is able to rise over the top of the AP particles with a lower titania concentration, which would allow for the combustion rate to be slowed. Since the titania reduces the binder melt layer but increases the oxidizer melt layer [28, 30], it is more difficult to limit combustion with high additive propellants.



**Figure 8 Combustion of a solid propellant with the addition of both a catalyst and the plateau additive. The image on the left represents a typical loading of nanoparticles (black dots) in the propellant. The image on the right represents a lower concentration of nanoparticles in the AP (grey spheres) and HTPB (yellow) propellants. With a higher amount of titania, the smaller AP particles are prevented from recessing into the binder. A lower amount of titania allows for the smaller AP to drop below the combustion line.**

By looking into the past research on plateau propellants, new methods were established toward realizing the goal to obtain a plateau propellant. This thesis took the information on the plateau mechanisms and sought to test new formulations. The literature suggests the way to obtain plateau propellants by altering the binder melt layer using different binders or curatives, adjusting the AP size and distributions, and including a burning rate modifier.

### 3. PROPELLANT FORMULATIONS

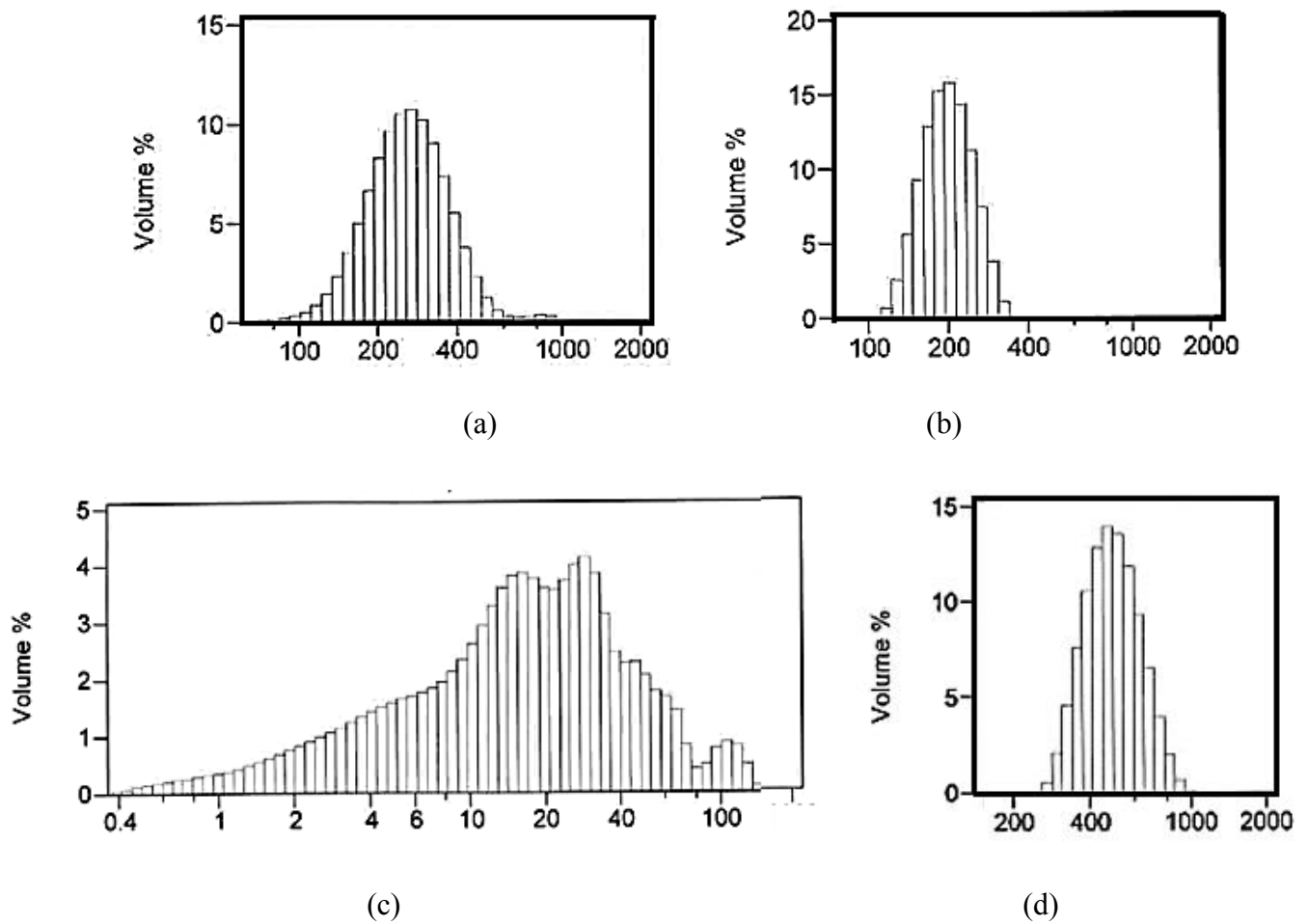
#### 3.1 Propellant Formulations

The focus of this thesis is on the combustion of a low-smoke, non-aluminized propellant. Propellants investigated are based on a baseline formulation containing five key components: oxidizer, fuel-binder, plasticizer, bonding agent, and curative [1, 31]. Ammonium perchlorate (AP) is used as the oxidizer, and R45-M hydroxyl-terminated polybutadiene (HTPB) acts as both fuel source and binder. AP is considered to be a monopropellant and can act as its own fuel source for combustion [1]. Dioctyl adipate ( $C_{22}H_{42}O_4$ ) is the plasticizer, and HX-752 Dynamar™ acts as a bonding agent; both improve the physical properties of the propellant by strengthening the structure of the propellant via cross linking of the hydrocarbon bonds. Isophorone diisocyanate (IPDI) is the curative to solidify the propellant slurry.

The propellants examined in this study consisted of AP in monomodal, bimodal, and trimodal particle size distributions, with the monomodal propellant being tested first. After examining the effects of the AP distribution in a monomodal propellant, tests were conducted on bimodal and trimodal mixtures with the addition of a non-catalytic additive. Finally, after the propellant was discovered to plateau using the AP distribution along with the non-catalytic additive, a catalytic additive was introduced. Plain titania was used to enhance the burning rate of the plateau propellant. Both pure and chemically doped titania have been found to produce higher-order burning rate increases with lower

oxidizer mass loadings compared to propellants with higher oxidizer mass loadings [32, 33]. For this study, only pure, un-doped titania was used and was provided by the team at UCF working in the AMPAC center.

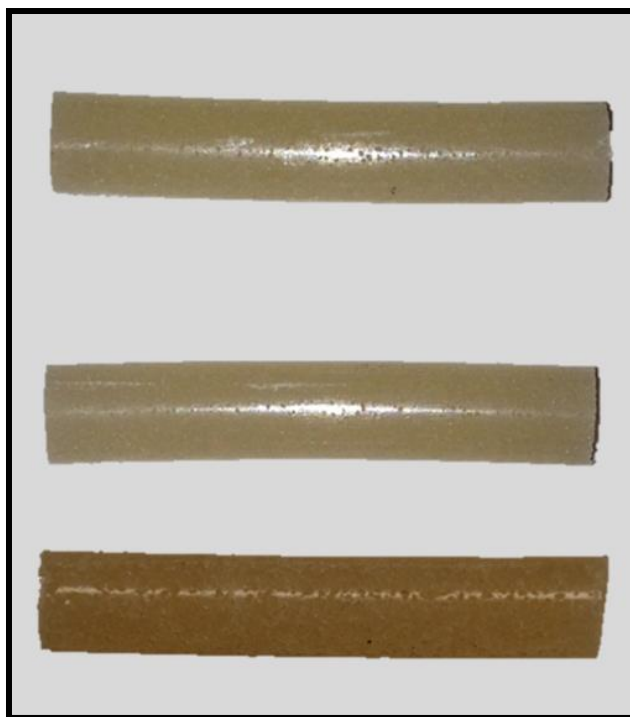
A propellant with the bimodal AP distribution was prepared by mixing two batches of AP with peaks at 23  $\mu\text{m}$  and 204  $\mu\text{m}$  at a ratio of 30/70 fine AP to coarse AP (by weight). For the trimodal formulations, the AP distribution was prepared by mixing three batches of AP with peaks at 23  $\mu\text{m}$ , 204  $\mu\text{m}$ , and 500  $\mu\text{m}$  with a ratio of 30/40/30 fine AP to coarse AP to large AP. The monomodal propellants contained 80% by mass coarse AP with a peak at both 204 and 280  $\mu\text{m}$ . Bimodal and trimodal propellants were formulated using an 85% by mass of oxidizer loading. Choosing to use 85% in bimodal propellants in this study was based on the fact that they are the most commonly used propellants in industry. The AP distributions used in the mixing of the propellants can be found in Fig. 9. Previous research has shown that overall AP size distribution, mass-loading, and modality all play roles in how well the propellant performs as well as how well the titania can be a burning-rate enhancer [32, 33, 34]. Additionally, the AP size distribution, mass-loading, and modality affect the burning of composite propellants on their own.



**Figure 9 AP size distributions provided by Fluid Energy Corp. (a) The wide distribution AP particles with a nominal diameter of 280  $\mu\text{m}$  and a standard deviation of 115  $\mu\text{m}$ . (b) The sieved distribution AP particles with a nominal diameter of 204  $\mu\text{m}$  and a standard deviation of 40  $\mu\text{m}$ . (c) The distribution of fine AP particles with a nominal diameter of 21  $\mu\text{m}$  and a standard deviation of 24  $\mu\text{m}$ . (d) A distribution large AP particles with a nominal diameter of 500  $\mu\text{m}$  and a standard deviation of 128  $\mu\text{m}$ .**

Propellants with smaller AP particles will burn faster than those with larger particles. The increase in burning rate is primarily driven by the relative change in flame structure seen with varying AP particle size. With smaller particles, the higher surface area-to-volume ratio promotes increased premixed flame structures compared to the diffusion flames seen with larger AP particles [35, 36]. The premixed flame dominates at the interface of oxidizer and binder while the diffusion flame is more focused above and near the center of the particle. The premixed flame burns hotter and faster, resulting in elevated bulk propellant deflagration rates

Figure 10 compares three samples of the physical propellants used in the study, and it should be noted that there is little difference in the appearance for each of the batches studied. The propellants shown are the 80% baseline and the 85% bimodal with the titania additive. Often times, the AP distribution is over looked or not published, but previous studies have shown how important the AP size distribution is to the combustion.



**Figure 10 Solid propellant test samples did not vary in appearance when comparing the baseline with the additive.**

There are several noteworthy features of Figure 10. First, the baseline and the titania propellants are nearly indistinguishable from one another. The yellowish color is from the yellow HTPB binder. The bottom sample shows the difference when dry titania powder is added to the propellant. Titania causes the propellant to become slightly yellowish/orange in color. It should be noted that all of the batch numbers were made with a non-catalytic additive in the propellant. Table 2 lists the propellant formulations of all of the propellants tested in this thesis.

**Table 2 Propellant formulations used in this thesis study.**

<b>Propellant</b>	<b>AP%</b>	<b>Modality</b>	<b>Catalyst</b>	<b>Plateau Additive</b>
Baseline	80%	Monmodal	-	No
Baseline	85%	Bimodal	-	No
Unsieved	80%	Monmodal	-	No
Batch 1	85%	Bimodal	-	Yes
Batch 2	85%	Bimodal	-	Yes
Batch 3	85%	Bimodal	-	Yes
Batch 4	85%	Bimodal	-	Yes
Batch 5	85%	Bimodal	-	Yes
Batch 6	85%	Trimodal	-	Yes
Batch 7	80%	Monmodal	1.00%	Yes
Batch 8	80%	Monmodal	0.10%	Yes

### **3.2 Propellant Mixing**

Over the past several years, the techniques for manufacturing laboratory-scale propellants in the author's laboratory have been continuously refined. Every step in the process is closely monitored and evaluated to ensure that the method is held to a high quality as well as routinely being updated with industry standards. The overall scatter of burning rate data is evaluated to determine whether a new mixing procedure involving nano-sized additives increases or decreases propellant uniformity.

Propellants are prepared using one of two methods: a procedure using a mechanical mixer developed by students in-house or a hand-mixing method. The mechanical mixer incorporates a heated, evacuated chamber that mimics large-scale manufacturing facilities and is presented in further detail by Stephens et al. [37].



Propellants presented in this thesis were manufactured according to the hand-mixing method. The hand-mixing procedure has been validated to produce consistent results that are identical to the mechanical mixer in a previous paper [37].

Hand mixing takes place under a Labconco fume hood to reduce the chance of exposure to harmful chemicals and vapors if combustion is initiated during mixing. Ingredients are mixed in a glass beaker with a glass stirring rod which has been sterilized using acetone to reduce variances between batches. Mixing in an inert container reduces the chance that an energetic chemical will react with the beaker or mixing rod, altering the chemical properties of the propellant, or causing premature combustion. A Baseline propellant slurry in the mixing beaker is shown in Figure 11.



**Figure 11 Image of a laboratory-scale, hand-mixed AP-HTPB propellant.**

Ingredients are weighed to within 0.01 g accuracy on a digital scale to maximize the repeatability of the formulation, and to allow for measurement precision in the order of 0.1% of the end propellant mass. One exception is for small quantities of additives (less than 1.0% by mass) since the smallest quantity of additive is often close to the precision of the scale. The general procedure that has been developed has been seen to maximize uniformity of the propellant matrix and repeatability in burning rate data.

During mixing, liquid ingredients are mixed before solids. The exception is the addition of the liquid curative which must be added shortly before the propellant slurry is compressed into test strands. Once an ingredient is added, it is mixed for at least ten minutes, and then placed in a vacuum chamber. While heating has been utilized in the mechanical mixer, hand mixes were not heated. A major change to the mixing procedure in the past year has been the addition of heating the mixture throughout the entire process. Heating the mixture to approximately 65 °C lowers the viscosity of the mixture, helping to ensure the solid particles are completely encased in binder. Using heat also aids in crushing the agglomerates in the solid ingredients and mimics the process used in the mixing large-scale facilities. Mixtures are evacuated for twenty minutes after the addition of each liquid ingredient, and for two hours after the addition of each solid ingredient. The vacuum stage helps to remove air pockets introduced during mixing, and when the mixture is heated the air pockets are able to travel faster. Air voids artificially inflate the burning rate as they reduce the combustible mass on a per volume basis. Vacuuming considerably increases mixing time but has been seen to increase uniformity

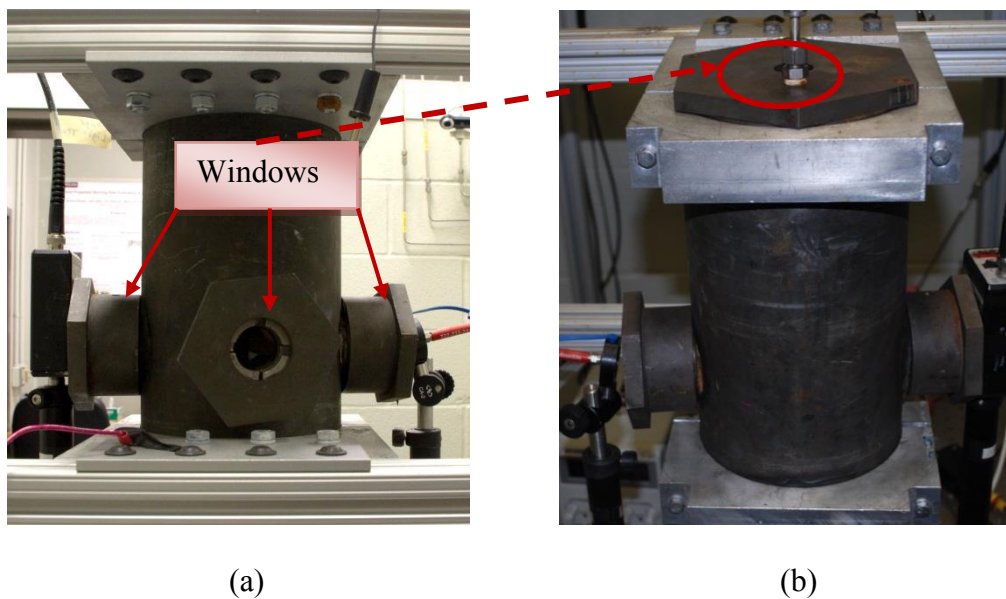
of the propellant matrix and reduces scatter in burning rates by decreasing the density. The density of each propellant sample is measured to ensure that the porosity variability is not excessive; with increased porosity in a propellant, the burning area is increased artificially inflating the burning rate observed.

The AP oxidizer is added during the solids-mixing stage starting with the smaller sizes and moving to the larger size as needed. Prior to mixing in the AP, the oxidizer batch is sieved twice to narrow the size distribution and prevent overly large or overly small particles from significantly affecting propellant burning trends. However, for this study three batches of propellant were made using the non-sieved AP to demonstrate how the naturally wide AP distribution can be used to create a plateauing propellant. Once all ingredients have been introduced and the mixture evacuated, the slurry is extruded into a Teflon® tube with an inner diameter of 0.1875 in. (4.76 mm). A long, cylindrical strand of propellant is produced and cut into short strands (about 1 inch long) leaving a quarter inch to ensure uniformity. Testable strands are placed into an oven and cured at 63 °C for 7 days. Once the propellant has cured, the strands are removed from the oven and prepared for testing.

## 4. TESTING PROCEDURES

### 4.1 Test Vessel

Propellants are tested in a constant-volume, high-pressure strand burner designed and built by previous students in the laboratory. The strand burner is rated for tests up to 8000 psi (55.2 MPa), but propellants are normally tested at pressures no greater than 3000 psi (17.2 MPa). The test area is cylindrically shaped with an internal diameter and length of 3.70 in. of 6.50 in., respectively. For testing, the strand bomb is oriented vertically, but the option to test horizontally is available. The installed strand bomb is shown from opposing perspective sides in Figure 12, with the spectrometer photon collector on the right of image (a).



**Figure 12 Strand-bomb test vessel.**

Propellant samples are mounted with the burning surface in-plane with the three lower windows, marked by the solid arrows as seen Fig. 12 (a). Having the propellants in-plane with the windows allows for spectrometer measurements of the combustion products. A fourth window looks down on the propellant sample burning surface, marked by the dashed arrow best seen in the downward view in Fig. 12 (b). The three in-plane windows are made of sapphire and are mounted in 316 stainless-steel housings.

All the work done in this thesis was performed in the Texas A&M University strand burner, and additional information on the strand burner design is found in the thesis by Carro [38]. The ambient room temperature is recorded prior to each day of testing as initial propellant grain temperature has an effect on the combustion rate of APCPs. The room temperature is maintained at temperatures between 20.0 °C and 21.5 °C to minimize temperature effects [2, 39].

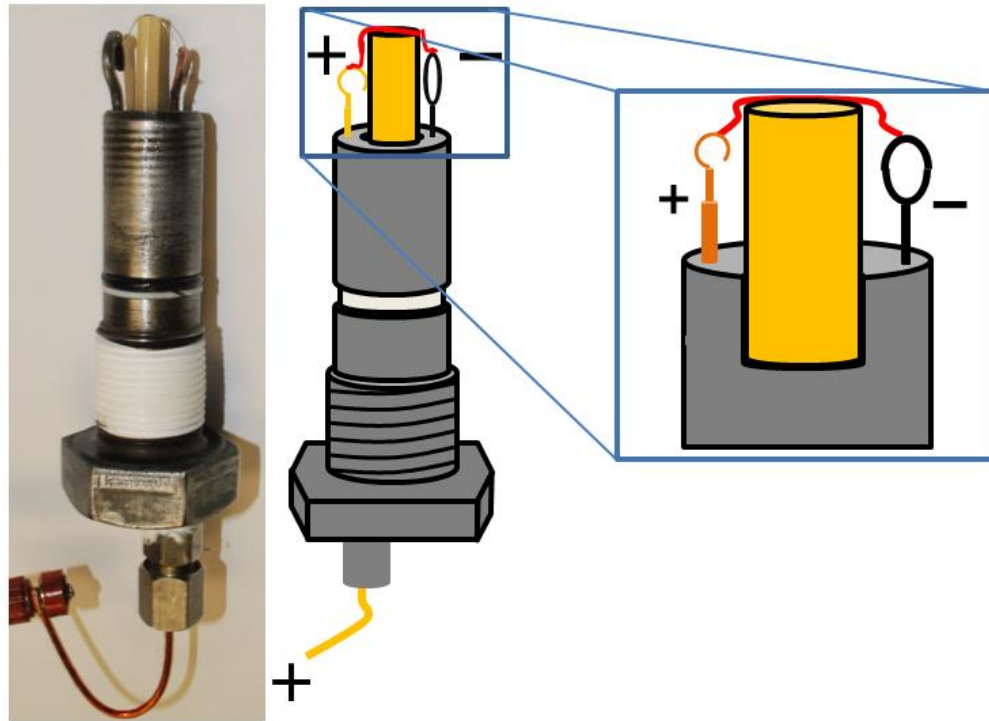
## **4.2 Sample Preparation**

Prior to testing, each sample is removed from its protective Teflon® sheath, weighed, and measured. A sample still in the Teflon coating is shown in Figure 13. The sample is approximately 1.25 in long. During sample preparation, a small fraction of the overall sample length is removed from each end to pare the sample down to approximately 1 inch in length. This procedure serves the dual purpose of creating consistently sized test samples, but more importantly, removes the propellant ends which have expanded outside the tube and are no longer cylindrical.



**Figure 13 Propellant sample in Teflon® sheath.**

Once the sample has been removed from its housing and cut down to an appropriate length, digital calipers are used to measure the sample length. Sample mass is measured to within 0.01 g by a digital scale. Once the size and weight are recorded, a liquid inhibitor is applied to the sidewalls of the propellant sample using a rolling method, and it is placed into the strand holder. A small Teflon collar is placed at the bottom end of the propellant sample to stabilize the propellant in the sample holder. A 30 BNC (0.01 in. diameter) Nichrome wire is laid across the exposed combustion surface of the sample, ensuring that the wire is flush with the propellant surface. The strand holder is screwed into the base cap of the strand bomb with the sample oriented vertically along its length; thread tape is added to improve the pressure seal for the bolt threads. A photograph and corresponding schematic of the strand holder with a prepared sample are shown in Figure 14.



**Figure 14 Propellant strand-holder photograph and schematic demonstrating how the propellant is mounted and the wire is set upon the propellant.**

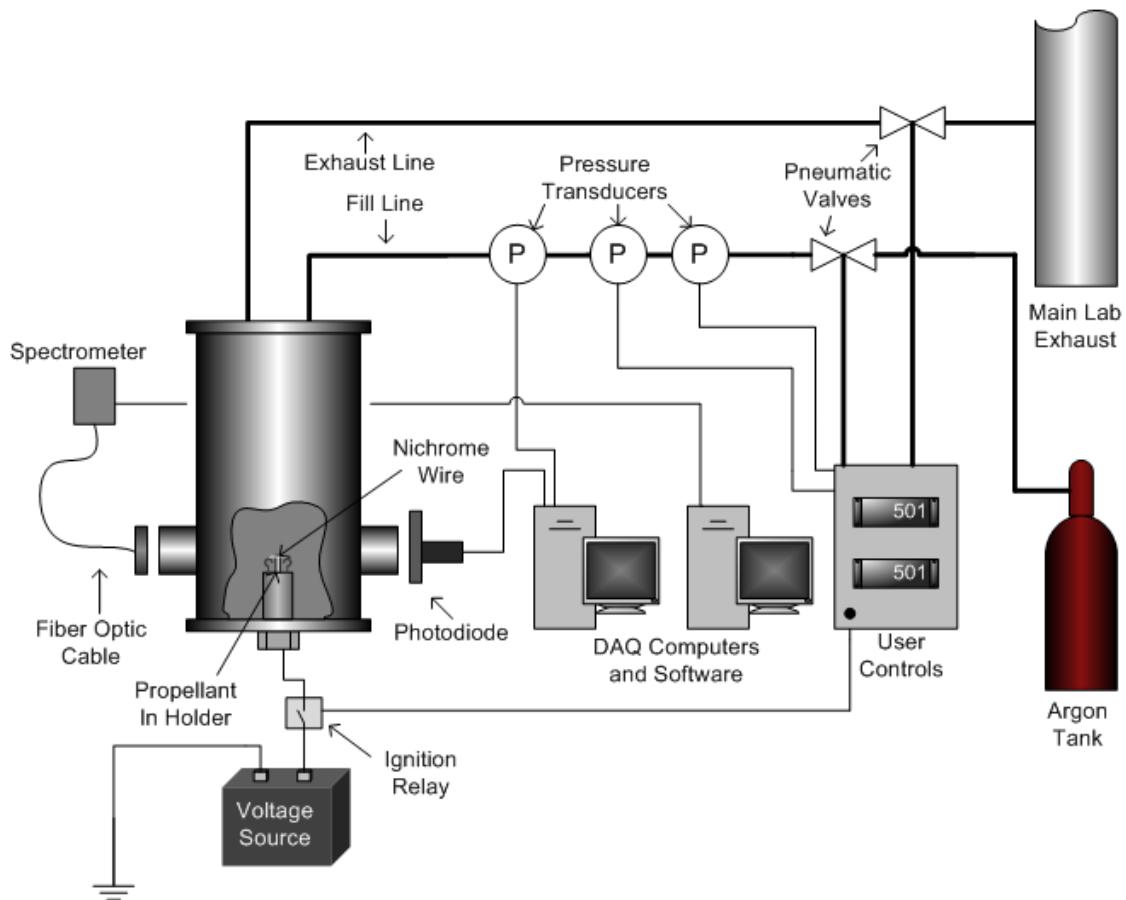
The magnification of the image illustrates how the wire rests on the propellant before being inserted into the bottom of the strand burner. Ignition of a solid propellant strand is by the combustion of a high energy wire which initiates the self-deflagration of the propellant. A common method to generate the activation energy is to attach a very thin metal wire, typically a nickel-chromium (Nichrome) metal blend, to the propellant. The wire must rest just inside the propellant surface, then a high voltage is run through the wire and the wire gets red hot just before it burns off. Before the wire disintegrates, the propellant ignites and self-sustaining combustion of the propellant is achieved.

With the closure of a digital relay, 6 amps of current are sent through the wire, and it quickly reaches temperatures of approximately 1000 °C, initiating combustion. To close the digital relay, a copper wire was purchased from Connex to be mounted on the bottom of the bolt. The copper lead has a coating as to not short circuit with the bolt prior to the grounding steal lead on the other side. Combustion temperatures well above 2500 °C then vaporize the wire, and the sample burns to completion. The strand holder can be easily screwed into or removed from the bottom of the test vessel, promoting quick turnaround times between tests. The strand holder is reusable and has lasted for over thousands of individual tests.

#### **4.3 Testing and Data Acquisition**

A schematic of the complete experimental setup is shown in Figure 15. During testing, the high-pressure lines and the strand bomb are isolated behind cinderblock blast walls filled with steel-reinforced concrete. Testing controls are managed remotely from a separate control room using the data acquisition board (DAQ) on the computers and the User Control board. This setup reduces the safety risk associated with working with high-pressure environments. If the strand-bomb were to rupture during the gas fill, sample test, or gas vent processes, researchers are protected by the blast walls and a fan ventilation system would remove any hazardous gases in the room. An additional manual safety vent valve is available in the case of power failure.



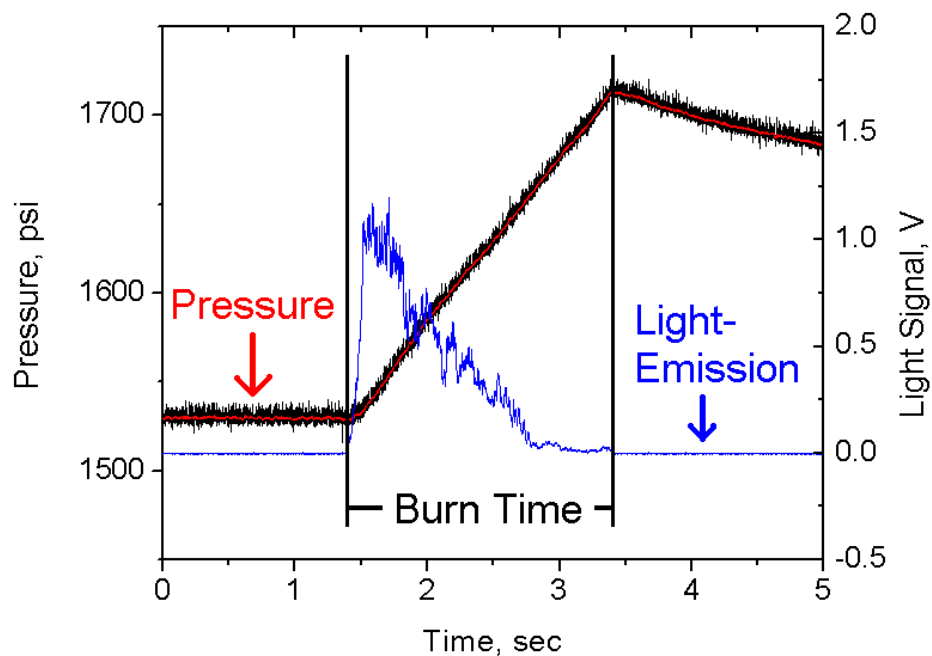


**Figure 15 Experimental schematic for solid propellant burning rate remote tests.**

Each formulation was tested over a range of pressures from 500 – 3000 psi (3.5 – 20.8 MPa) to replicate the high pressures seen in a rocket motor during use. During a test, the strand bomb is pressurized using inert argon gas. Inert gases are used as they do not affect the combustion process. Another popular choice in propellant diagnostics is nitrogen, but argon has a lower heat capacity resulting in less heat lost to the environment. There are three pressure transducers incorporated into the experimental apparatus to ensure higher pressure measurement reproducibility. The first is used for the

data acquisition described below; the second displays real-time strand bomb pressure to researchers in the experiment control room to monitor whether the combustion of the propellant was achieved; and the third is used to calibrate the first two transducers. The DAQ and display transducers are calibrated at the beginning of each testing day. The calibration transducer is isolated from the strand bomb during testing to prevent fouling by the combustion products.

Pressure, light intensity, and spectral data are collected during sample burning. Pressure and light-emission data are collected using a computer-based data acquisition board from Gage Applied Sciences run by the GageScope software package at a sampling rate of 1 kHz. Strand bomb pressure is recorded with an OmegaDyne PX02C1-7.5KGI pressure transducer and calibrated using the same pressure transducer. A Focus model 2031 broadband photoreceptor is used to detect the intensity of the light emission. Burning time is determined with the pressure response and validated with the light-emission trace. Sample pressure and light traces are shown in Figure 16.



**Figure 16 Sample pressure and light-emission data plot taken from experiments.**

There are three important factors to note about the plot in Figure 16. First is that data smoothing is done by applying a Savitzky-Golay polynomial smoothing filter to the pressure trace to reduce high-frequency noise in the transducer response. Noise is generated from the power outlet in the test cell. A smoothed pressure response is plotted as a red line within the original noisier trace in black. Test time, or “burn time,” is determined to be the time the observed between ignition and propellant burn out. Ignition is marked when a pressure rise is observed, and burn out is given by the point at which the pressure reaches a maximum and begins to decay; both are verified using the light trace. Tests where the times determined from the pressure and light-emission varies by ~5% or greater are disregarded.

## 5. DATA PROCESSING AND UNCERTAINTY

### 5.1 Data Processing

Data collected from the testing is completely useless if there is not a method to evaluate the raw data. Since the propellant strands are measured prior to testing, the burning rates are determined as a simple rate function of sample length over burn time. Time is approximated from the methods described in the previous section. Equation 4 is used to calculate individual sample burning rates, with  $r$  representing the linear burning rate,  $l$  the initial sample length and  $\Delta t$  the burn time. The burning time is acquired from the dynamic pressure measurement of the pressure and assumes complete combustion of the propellant sample.

$$r = \frac{l}{\Delta t} \quad (4)$$

Burning rate data are plotted on a log-log plot as a function of test pressure. The mass of the propellant must be large enough to extract a reliable data trend, but not too high as to cause overly large pressure increases. Propellant burning rate is typically a function of pressure, but the pressure is increased during the constant-volume burn. If the pressure increase is too high, the data become unreliable. Test pressure must be evaluated as the mean from the initial and final pressures recorded during the test time to account for the pressure variation.

## 5.2 Uncertainty Analysis

Uncertainty in the data is inherent when measurements of any type are made, and the error from these measurements must be determined. Variability and uncertainty in the calculated burning rate correlation constants are from a variety of sources. The primary sources of variability in the burning rate constants are the natural combustion fluctuations and variability in mixture uniformity from batch to batch. A minimum of ten samples are burned for each propellant batch so as to minimize the effects of variation in mixture uniformity. Each sample's density and overall uniformity are evaluated from physical measurements of the mass and length. Density variations can account for larger-than-normal scatter; lower densities signal the presence of air voids which will inflate the burning rate. Error bars representing 10% error in the measurements are generally plotted along with burning rate. A least-squares regression correlation is used to better represent the scatter observed in the tested propellant batches. Uncertainty stems from the measurements for both sample length and mass, adding to the additional level of ambiguity to the burning rate correlations.

Total measurement uncertainty was determined using the root-sum-square (RSS) method from the individual measurements of the pressure/light traces, sample length/mass, and time resolution. Since there is no correlation between the instrumentation errors, the RSS method serves as a sufficient method in determining the uncertainty amongst the data. Tolerances in the sample length and mass measurements

as well as burn time were found to be  $\pm 0.005$  in. (0.125 mm),  $\pm 0.01$  g, and  $\pm 0.032$  s, respectively. Using a root-sum-square (RSS) approach on the minimum and maximum burning rates observed, the value for the combined uncertainty in burning rate was found to range from 3.3% to 4.3%. The uncertainty in the DAQ pressure transducer is 0.15%, as reported by the manufacturer, which amounts to less than 1 psi at the lower end of the pressure range (500 psi, 3.5 MPa) and 4.5 psi at the upper end (3000 psi, 20.8 MPa). These numbers are compared to a calibration pressure transducer and found to agree with the variation in pressure measured with the calibration.

A comparison of the theoretical density and the average density of the propellant results in an average error within 90% of the theoretical density. To maintain strict quality control from batch to batch and evaluate if a seemingly bad data point should be removed or treated as scatter, the density is closely monitored. Table 1 shows the comparison of the densities for the propellants studied in this study. Propellants with a density differing from the theoretical value by more than 85% are discarded because their air content is too large and would artificially inflate the burning rate.

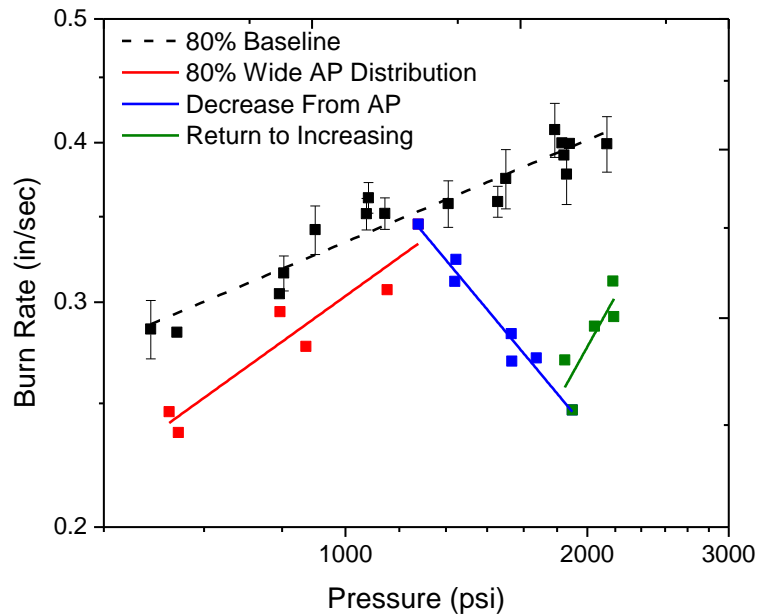
**Table 3 Uncertainty calculated from the comparison of the theoretical density and the actual density of the propellant.**

<b>Batch</b>	<b>Theoretical</b>	<b>Actual</b>	<b>%Theoretical</b>
Baseline	1.59	1.46	91.82%
Bimodal	1.65	1.47	89.09%
Trimodal	1.69	1.55	91.72%
Catalytic Additive	1.61	1.41	87.58%
Average			90.05%

## 6. PLATEAU PROPELLANT DATA

Experiments were performed to determine if different propellant formulations would cause the plateau burning behavior. using wide distributions of AP in a propellant and then burning it repeats previous works over the last century, mesa burning was achieve in the propellant [5-11]. Next, experiments were performed by adding other typical ingredients intended to induce the plateau effect. Propellant burning rates were plotted against the baseline formulation for that propellant, comparing the burning trend to see how the new formulations altered the baseline. In general, the plateau propellant formulations were successful in achieving a period of pressure insensitivity.

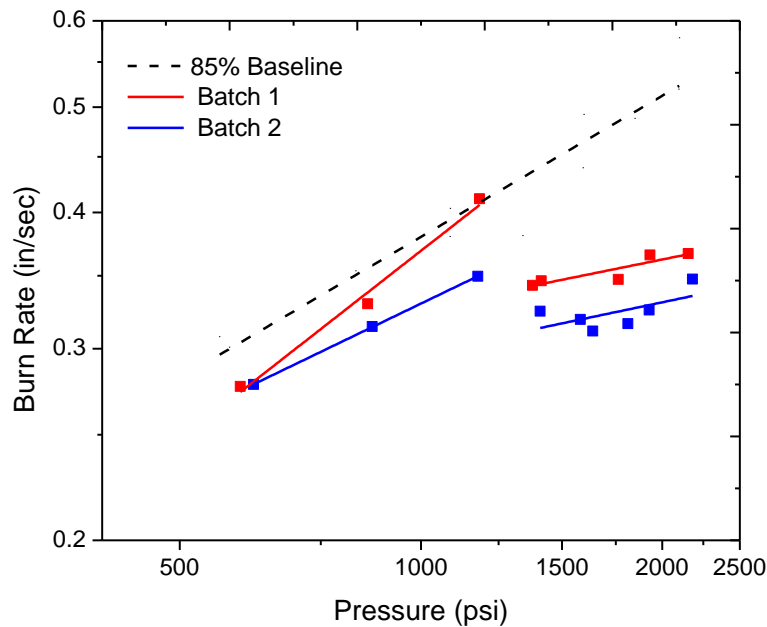
Figure 17 presents the burning rate data for the first two propellants tested. The 80% baseline propellant had sieved AP particles, while the 80% wide-AP propellant contained the un-sieved AP batch listed in table 1. The un-sieved AP produced a burning profile that is common for propellants with wide AP distributions, i.e., more of a mesa burning profile. The red region is the standard increase seen at lower pressures; blue is the decreasing burning rate region due to the washout of the smaller particles; green is the return to increasing with pressure. It is also important to note that the wide AP distribution also shifts the propellant burning rate to smaller overall values than the baseline formulation that contains the sieved AP particles.



**Figure 17 Plot of the 80% baseline using a wide distribution of AP compared to the typical sieved AP batch. Negative pressure dependence ( $dr/dp$ ) was achieved using a wide AP distribution.**

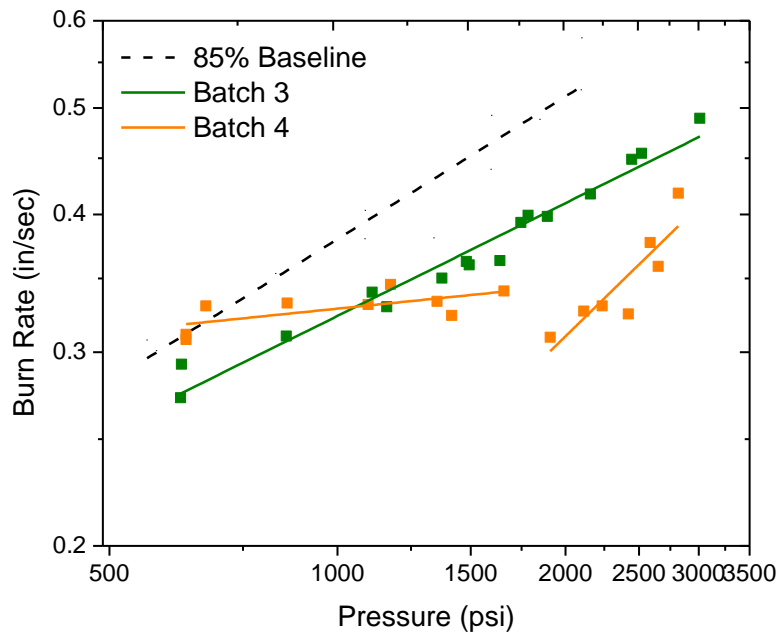
Trends seen in the baseline comparison for wide AP distribution are consistent with past studies by Boggs and Beckstead [24, 25]. Figure 18 presents the burning rate data for the 85% bimodal mixture where the non-catalytic additive was introduced to the batch containing a wide AP particle size distribution. Batch 1 contained normal concentrations of the additive, while Batch 2 contained a slightly larger dose, and it should be noted that the propellants exhibited a region of near-plateau behavior for pressures between 1250 to 2250 psi.





**Figure 18 Propellant using 85% bimodal mixture with the additive to initiate the plateau effect. Using the wide distribution of AP resulted in a near-plateau profile. Batch 1 contains normal concentration of the additive, and Batch 2 contains a slightly higher concentration (see Table 1).**

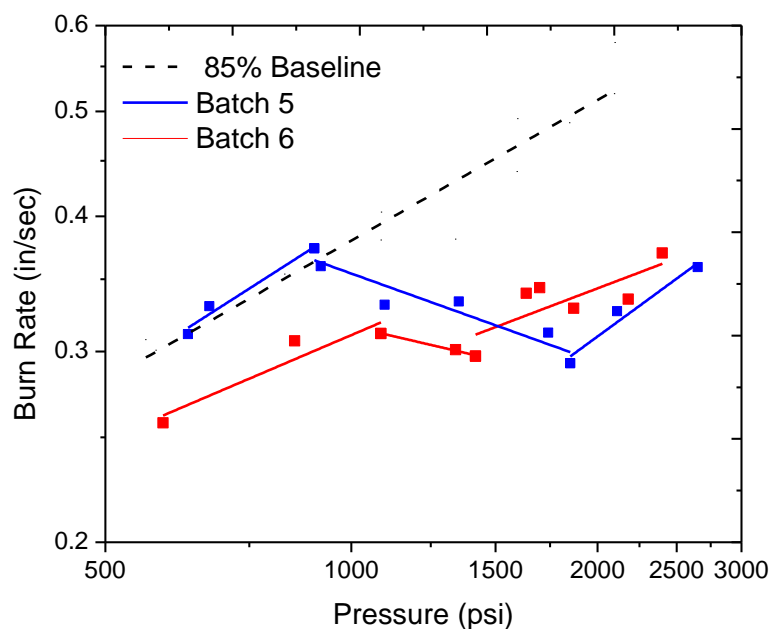
Figure 19 presents the burning rate data for the same 85% bimodal mixture with the non-catalytic additive, but the batch was mixed with a standard-sieved batch of AP with a narrow size distribution. Batch 3 containing normal concentrations of the additive exhibited a linear burning behavior, and the additive did not cause a plateau in any of the tested pressure regions. Batch 4 containing more additive exhibited a region of plateau-like burning at lower pressures ranging from 500 to 1750 psi. The results showed that insufficient quantities of additive would prevent the plateauing behavior, while additives above a certain amount could induce a plateau-like behavior.



**Figure 19 Propellant using 85% bimodal mixture with the additive to initiate the plateau effect. Using the standard sieved distribution of AP resulted in plateau profile for one but for the other, the additive was not enough to plateau. Batch 3 contains normal concentration of the additive, and Batch 4 a slightly higher concentration.**

With the knowledge that AP distribution can directly cause the plateau effect on a propellant, new trimodal mixture propellants were manufactured. The intent was to widen the AP distribution using oxidizer particles that have been strictly regulated to produce a plateau propellant. Figure 20 presents the burning rate data resulting from the testing of 85% bimodal and trimodal propellants containing more of the non-catalytic

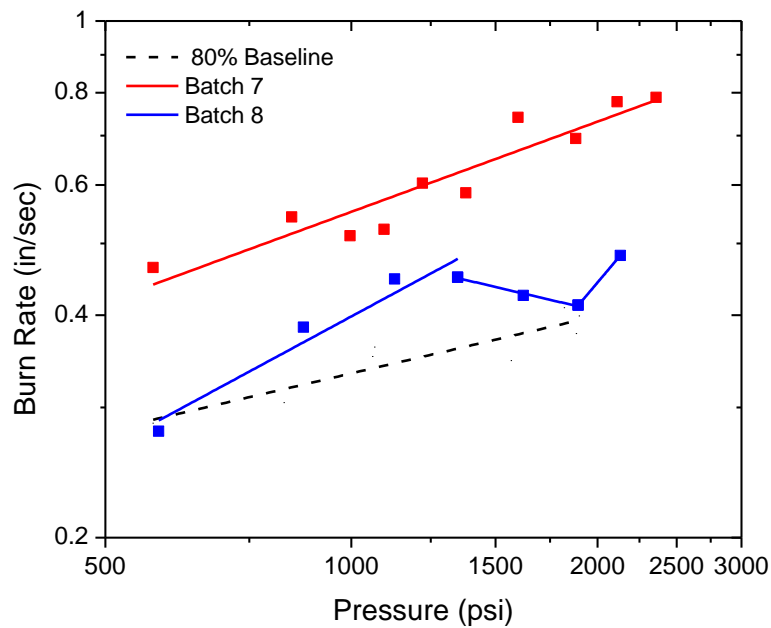
additive. These propellants exhibit quasi-plateau properties because there is slight negative pressure dependence rather than the flat pressure dependence seen in a plateau burning profile. The trimodal propellant, batch 6, produced a region of quasi-plateau from 1000 to 1500 psi, while batch 5, the bimodal propellant, quasi-plateaued at 800 to 1750 psi.



**Figure 20 Propellant with sieved AP at 85% using the non-catalytic additive with both bimodal and trimodal mixture to plateau the propellant. Batch 5 is the bimodal propellant mixture and batch 6 is the trimodal propellant.**

Once the plateau-like behavior was achieved with adding more of a typical ingredient, a metal oxide catalyst was added to the mixture. In an effort to shift the plateauing propellant burning rate to a faster regression, titania was added to the batch.

Both concentrations of 1.0% and 0.1% of titania were added to test if the plateau effect would be masked by the catalysis from the additive on propellant. Figure 21 illustrates how the titania both masks and improves the burning performance of the plateau propellant.



**Figure 21 Results from the plateau additive combined with the titania to check if plateau could have an elevated burning rate. Batch 7 is the propellant with 1.0% titania, and batch 8 contains 0.1% titania.**

From the above graph, using 1.0% titania, the red line, in the propellant masks the performance of the plateauing additive. The blue line shows that at a 0.1% concentration of titania, the plateau additive is still capable of producing the desirable burning profile and shifted the region to a higher burning rate.

In summary, these results show the effects of using an AP oxidizer that was not sieved and the use of a non-catalytic additive on the burning rate. Un-sieved AP has a wide particle size distribution and, according to past literature, causes propellants to exhibit plateau-like behavior. When coupled with a propellant additive, various particle sizes cause propellants to plateau at different pressure ranges. After the propellant plateaus in the bimodal mixture, a new formulation using a trimodal mixture was manufactured resulting in a propellant formulation that had a small plateau region. The intent was to investigate whether the larger particles would protrude through the binder melt layer and limit the plateau or enhance the plateau by completely smothering the smaller particles left in the binder. Seeing that the plateau effect could be achieved with a variety of methods, the catalytic additive titania was introduced to the propellant mix. Titania has been used by the author's group in the recent past, as an additive to increase the burning rate of propellants. The purpose was to examine if the plateau region could be shifted up to a higher burning rate at a given pressure. The results showed that with a normal dose of titania the plateau would be overpowered by the catalyst. Reducing the amount of titania is the method used in this study to achieve a plateau propellant with a catalyst, and still increase the burning rate of the propellant without a catalyst

## 7. CONCLUSION

This thesis presented a review of past research that contributed to understanding the plateau mechanism in propellants. Outlining the research on the binder melt layer and its effect on the viscosity and structure of the burning propellant, this thesis sheds light on the work of plateau propellants. Extensive amounts of research have been done on the AP size distribution of propellants enacting the plateau behavior in standard AP-HTPB propellants. Then the research examined how the binder melting temperatures changes depending on the type of binder and curative used. It was determined for HTPB binders that DDI would melt before IPDI, allowing for more of the AP particles to be washed out by the melt layer, slowing combustion. The literature also indicates that the inclusion of burning rate modifiers, such as metal oxides, can help to increase the binder melt layer at intermediate pressures which can cause a propellant to exhibit plateau behavior [11-16]. Over all, the study showed good agreement with the theories presented in the literature.

In this thesis, the results showed that the melt layer had a large impact on propellants made with a wide particle size distribution of AP for monomodal propellants. Showing that the wide distribution can result in a mesa burning for a baseline propellant, the same AP distribution was then applied to a propellant with a non-catalytic additive. Bimodal propellants were tested with the addition of a non-catalytic additive which allowed for the propellant to plateau. The results show that the plateau effect can be

established with a bimodal propellant, which could best be explained by the binder melt layer. It can be concluded that the mechanism that best describes the effect of the additive is that it lowers the viscosity of the melt layer. With a lower propellant viscosity, the AP crystals can recess further down in the melt layer, thus inhibiting the burning process and allowing the plateau-like behavior to happen. This theory of a lower viscosity agrees with past studies in the literature stating that a lower viscosity in the binder melt layer will result in a propellant exhibiting plateau burning [19-23]. When the trimodal propellants are burned, the largest particles protrude further into the combustion zone, thereby reducing the plateau effect of the additive. When the titania catalyst is mixed into the propellant, it allows the binder melt layer to return to a higher viscosity than the baseline. With the elevated viscosity, the plateau effect is removed, and no benefit is found from the primary additive. In smaller concentrations, the titania is shown to improve the burning rate and decrease the plateau region of an AP and HTPB propellant.

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